

The Significant Electronic Effect of the Imido Alkyl Substituent in d^0 Group 5 Imido Compounds Observed by Luminescence in Fluid Solution at Room Temperature

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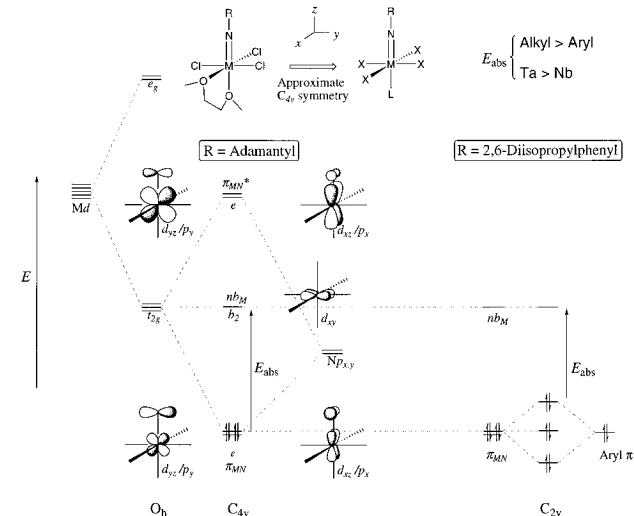
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Room temperature luminescence in fluid solutions from d^0 transition metal complexes is exceedingly rare. Only a few examples have been reported to date, including $\text{Cp}^*\text{TaCl}_3\text{X}$ ($\text{X} = \text{Cl}^-$, RCO_2^-),² and very recently, $\text{Ta}(\text{N}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{Cl}_3\text{L}_2$ ($\text{L} = \text{ether}$, amine).³ In these series, the emitting state has been attributed to a ligand to metal charge transfer (LMCT) from the cyclopentadienyl ligand (${}^3[\text{M} \leftarrow \text{Cp}^*]$) or imido ligand (${}^3[\text{M} \leftarrow \text{NAr}]$). In each case, emission energies are high ($\sim 16000\text{--}19000\text{ cm}^{-1}$) and rate constants for excited state decay range from approximately 10^3 to 10^7 s^{-1} . These data compare favorably with those reported for group 7 and 8 polypyridyl complexes $[\text{Re}(\text{L})(\text{CO})_3\text{X}]^+$ ^{4–8} and $[\text{ML}_2\text{X}_2]^{2+}$ ($\text{M} = \text{Ru}$, Os ;^{6,8–11} $\text{L} = \text{polypyridyl ligand}$, $\text{X} = \text{Lewis base}$).

We have prepared and examined a series of group 5 imido compounds of the form $\text{M}(\text{NR})\text{Cl}_3\text{L}_2$ ($\text{M} = \text{Ta}$, Nb ; $\text{R} = \text{phenyl}$, 2,6-diisopropylphenyl, *t*-butyl, 1-adamantyl; $\text{L}_2 = \text{py}_2$, 1,2-dimethoxyethane)^{3,12,13} to demonstrate the large alkyl effect on electronic structure. The geometry of these species (Scheme 1) as determined by ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra at room temperature (CD_2Cl_2) is clearly octahedral with a meridional arrangement of the chloride ligands, all *cis* to the imido ligand.^{12,14} The isostructural nature of these compounds allows a direct comparison of their spectroscopic and excited state properties.

The lowest energy absorption maxima for **1–8** in dichloroethane solution at room temperature vary dramatically over a range of about $10\,000\text{ cm}^{-1}$ (Table 1). We observe an increase of $\sim 2800\text{ cm}^{-1}$ in the lowest energy absorption upon changing the metal from niobium to tantalum. An increase of $\sim 6000\text{ cm}^{-1}$ is apparent upon changing the imido substituent from 2,6- $\text{iPr}_2\text{-C}_6\text{H}_3$ (**5**, aryl) to adamantyl (**1**, alkyl). It is profound that the absorption energy varies more dramatically as R changes than as M changes, indicating the intimate electronic interaction between $\text{Np}_{x,y}$ and $\text{Md}_{x,z,yz}$, Scheme 1. Making a similar change,

Scheme 1. Pertinent Orbital Interactions in the Lowest Energy Absorptions for Compounds **1–8**



alkyl ($\text{X} = \text{CH}_3$) to aryl ($\text{X} = \text{Ph}$), in $\text{Re}(4,4'\text{-X}_2\text{-bpy})(\text{CO})_3\text{Cl}$ results in a lowering of the MLCT absorption maximum by only 1500 cm^{-1} .⁵

The intensity of these transitions are suggestive of LaPorte forbidden ligand field transitions, with the complication that there are (formally) no d electrons!¹⁵ The ligand field model predicts (assuming a higher local C_{4v} symmetry at the metal) that the b_2 (d_{xy}) orbital is lowest in energy, Scheme 1. This is due to significant compression along the z axis ($\text{Ta-N}(\text{imido})$ bond distances are typically $\sim 1.75\text{ \AA}$ in octahedral environments).¹⁴ There is a significant covalent π interaction between e (d_{xz}, d_{yz}) and $\text{Np}_{x,y}$ that stabilizes the high oxidation state of the metal in these complexes. The HOMO–LUMO absorption should be orbitally allowed (Scheme 1), but the low intensity ($200\text{ M}^{-1}\text{cm}^{-1} > \epsilon > 20\text{ M}^{-1}\text{cm}^{-1}$) of these transitions is consistent with a spin-forbidden absorption, ${}^3(\text{nb}_M \leftarrow \pi_{\text{MN}})$, which gains intensity through spin–orbit coupling. The larger shift in the transition energy upon variation of the imido substituent compared to that observed upon variation of the metal is consistent with a highly covalent bonding picture, since the energy of $\text{Np}_{x,y}$ varies significantly as R changes from alkyl to aryl. This is due to mixing of the aryl π system with the M-N π bond, Scheme 1. The M-N π -bonding orbital is split into separate combinations, one in which mixing from the aryl π system is significant. This lowers the HOMO–LUMO energy separation and the lowest energy absorption.

Excitation into the lowest energy ${}^3(\text{nb}_M \leftarrow \pi_{\text{MN}})$ absorption in compounds **1–8** results in generation of a relatively long-lived excited state which is luminescent at room temperature in fluid solution. In each case the absorption and emission bands are essentially mirror images, suggesting emission from the state attained upon absorption. Excitation spectra match absorption spectra in each case, as reported earlier for **5** and **6**.³ The exception is **8**, from which no significant emission is observed. The Stokes' shifts are quite large and are consistent with a larger excited state distortion for the alkyls compared to the aryls.^{8,9,16–18}

There is a very large increase in emission energy upon substituting alkyl for aryl. We observe a drop of 2 orders of magnitude in quantum yield and almost 3 orders of magnitude in excited state lifetime upon substitution of aryl (**5**) for alkyl

(15) The nitrogen ligand here is considered an imido (RN^{2-}), making the metal d^0 , but it can also be considered a nitrene (RN) with a d^2 metal, in which case a LF assignment is reasonable.

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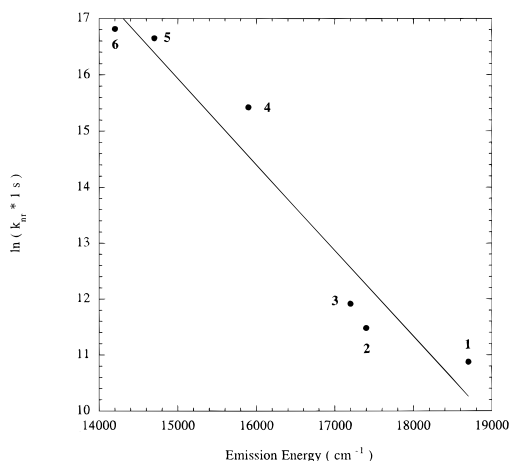
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Table 1. Spectroscopic Data for M(NR)Cl₃L₂^a

compound	E_{abs} , cm ⁻¹ (ϵ , (M cm) ⁻¹)	E_{em} , cm ⁻¹	τ , ^b ns	Φ_{em} ^c	k_{nr} , 10 ⁶ s ⁻¹	k_{r} , 10 ⁴ s ⁻¹
Ta(NAda)Cl ₃ dme (1)	28 400 (160)	18 700	15 100	0.20	0.053	1.3
Ta(N ^t Bu)Cl ₃ py ₂ (2)	26 800 (144)	17 400	9 350	0.096	0.097	1.0
Ta(NAda)Cl ₃ py ₂ (3)	26 500 (180)	17 200	6 000	0.095	0.15	1.6
Ta(NPh)Cl ₃ dme (4)	23 800 (112)	15 900	200	0.0041	5.0	2.1
Ta(NAr)Cl ₃ dme (5)	22 400 (128)	14 700	60	0.0012	17	2.0
Ta(NAr)Cl ₃ py ₂ (6)	20 900 (99)	14 200	50	0.0008	20	1.6
Nb(NAda)Cl ₃ dme (7)	25 800 (76)	15 400	3 000	0.010	0.33	0.33
Nb(NAr)Cl ₃ dme (8)	19 000 (34)	(11 500) ^d				

^a All data obtained in optically dilute dichloroethane solutions. Emission data were collected on a Spex Fluorolog emission spectrophotometer and were corrected for spectrometer response. ^b Determined using 440 nm excitation from a PRA LN1000/LN107 nitrogen/dye laser combination. ^c Obtained using an aerated acetonitrile solution of Ru(bpy)₃²⁺ ($\Phi_{\text{em}} = 0.012$) as an actinometer. ^d Calculated from the observed $\Delta E_{\text{em}} = (E_{\text{em}(1)} - E_{\text{em}(5)})$, assuming the same ΔE_{em} for **7** and **8**. This emission would be beyond the limit of detection of our spectrometer.

**Figure 1.** Energy Gap Law plot for compounds 1–6.

(1). This is due primarily to a decrease in the rate of nonradiative decay (k_{nr}) (Table 1). More significantly, the rate of nonradiative decay decreases systematically as emission energy increases in **1**–**6** (Figure 1).

The rate constant for nonradiative decay is proportional to the emission energy

$$k_{\text{nr}} \propto \exp\left[\frac{-\gamma E_0}{\hbar\omega_{\text{M}}}\right] \quad (1)$$

$$\gamma = \ln\left(\frac{E_0}{S_{\text{M}}\hbar\omega_{\text{M}}}\right) - 1 \quad (2)$$

where E_0 is the energy gap between the ground and excited states, S_{M} is the Huang–Rhys factor (a dimensionless distortional parameter), and $\hbar\omega_{\text{M}}$ is the medium frequency acceptor mode which contributes to excited state decay.^{8,9,16,17} In these systems nonradiative processes dominate excited state decay (Table 1). Equation 1 predicts an increase in k_{nr} as E_0 decreases. The observed correlation (Figure 1) suggests that the dominant

acceptor mode is *relatively* invariant in this series, despite the significant difference in the Stokes' shift calculated from the electronic spectra.

There is a large decrease in k_{r} from tantalum to niobium, consistent with larger spin–orbit coupling in tantalum, which increases the intensity of the transition by more efficient mixing of singlet and triplet states compared to niobium. Radiative rate constants vary within error as the alkyl group or Lewis base ligand is changed.¹⁹

These observations suggest that profound insight into the electronic structure of transition metal complexes containing multiply bonded ligands is available through electronic spectroscopy, similar to observations made earlier in other high oxidation state (d^0 or d^2) complexes containing multiply bonded ligands.^{2,18,20–23} A key observation is that the rate of nonradiative decay *apparently* follows energy gap law considerations.

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Supporting Information Available: Preparative details and data for compounds **1**–**8** (4 pages). Ordering information is given on any current masthead page for ordering and Internet access instructions.

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(19) The observation of the ${}^3(\text{nb}_{\text{M}} \leftarrow \pi_{\text{MN}})$ transition allows the calculation of k_{r} from the absorption band profile. Following Meyer,⁹ k_{r} is given by

$$k_{\text{r}} = (3.05 \times 10^{-9}) \eta^2 \langle \bar{\nu}^{-3} \rangle^{-1} \frac{\epsilon_{\text{max}} \Delta \bar{\nu}_{0,1/2}}{\bar{\nu}_{\text{max}}}$$

where η is the refractive index of the solvent, ν is the energy of emission, ϵ_{max} , $\bar{\nu}_{\text{max}}$, and $\Delta \bar{\nu}_{0,1/2}$ are the extinction coefficient, energy, and full width at half-maximum of the absorption band. Thus k_{r} (calcd) values for **1**, **5**, and **7** are 4×10^5 , 9×10^5 , and 3×10^5 s⁻¹.

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